বিদ্যাসাগর বিশ্ববিদ্যালয়

VIDYASAGAR UNIVERSITY

Question Paper

B.Sc. Honours Examination 2023

(Under CBCS Pattern)

Semester — II

Subject : CHEMISTRY

Paper : C–4T

(Organic Chemistry—II)

Full Marks : 40

Time : 2 hours

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Answer from **all** the Groups as directed.

GROUP—A

1. Answer *any* **five** questions from the following : 2×5=10

(a) Write the differences between torsional angle and dihedral angle.

(b) Give an example of *(i)* an asymmetric allene and *(ii)* molecule having stereogenic centre but achirotopic.

(c) Draw the conformational energy diagram of chloroethane with respect to C — C bond.

(d) *N*,*N*-dimethylation of aniline triples the basicity of aniline but *N*,*N*-dimethylation of 2,6-dimethylaniline increases its basicity by 30000 times. Explain.

(e) Butane-2,3-dione remains almost cent percent in keto form but cyclopentane-1,2-dione remains almost cent percent in enol form. Explain.

(f) *D* and *L* stereoisomers are not necessarily enantiomers. Illustrate your answer with suitable examples.

(g) Comment on the chirality and optical activity of $CH_3CH_2CH_2N(CH_3)CH_2CH_3$ and its corresponding *N*-oxide.

(h) How can E1cB pathway be distinguished from the kinetically indistinguishable E2 pathway?

GROUP—B

Answer *any* **four** questions from the following : 5×4=20

2. *(a)* Compare the basicities and nucleophilicities of NH_3, NH_2NH_2 and NH_2OH with suitable explanation. 3

(b) Hydrolysis of methyl iodide takes place at a much faster rate in presence of sodium iodide. Explain with energy profile diagram. 2

3. *(a)* Write the structures of keto and stable enol forms of 2,4-pentanedione. 1

(b) What are the factors that stabilize these enol forms? 2

(c) Account for the observation that enol content of this dicarbonyl compound is 92% in *n*-hexane and 15% in water. 2

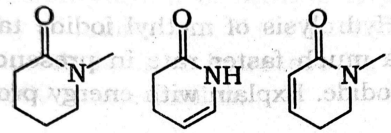
4. *(a)* Give the products with the configurational descriptor (R/S), in the following reactions. Explain their formation mechanistically. 3

(R)-2-Bromopropanoic acid $\xrightarrow{\text{Conc. NaOH}}$?

(R)-2-Bromopropanoic acid $\xrightarrow{\text{Moist } Ag_2O}$?

(b) Account for the observation that in DMSO the order of reactivity of halide ions with methyl bromide is $F^- > Cl^- > Br^- > I^-$, which is opposite to that observed in methanol solution. 2

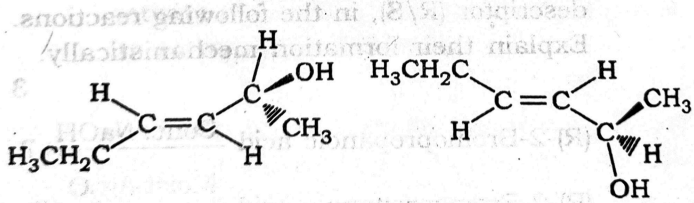
5. (a) Arrange the following amides in increasing order of basicity : 3

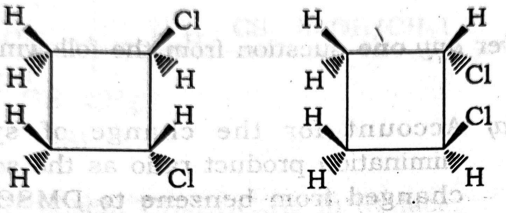


(b) (E)-isomer of $HO_2CHC = CHCO_2Na$ is a stronger base than its corresponding (Z)-isomer. Explain. Also comment on their relative acidities. 2

6. (a) How would you resolve (+/–) $CH_3CH(OH)CH_2CH_3$? 2

(b) Label the following pairs of the compounds as homomers, enantiomers and diastereomers : 2





(c) What is Troger's base? 1

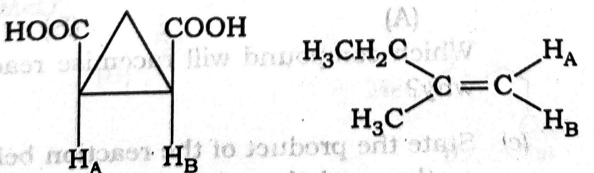
7. (a) $CH_3CHClCH_3$ and $CH_3CHClCH_3$ show kinetic isotope effect during : 3

(i) Substitution reaction using CH_3COOAg/CH_3COOH and

(ii) Elimination reaction using NaOMe/DMSO

Indicate the primary/secondary nature of the kinetic isotope effect in the above reactions explaining the variation of rate.

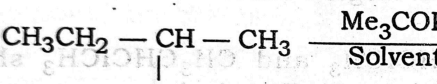
(b) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic and diastereotopic ligands. 2



GROUP—C

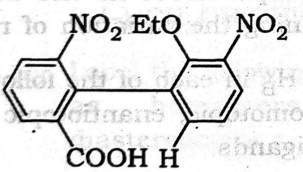
Answer *any* **one** question from the following : 10×1=10

8. *(a)* Account for the change of syn/anti elimination product ratio as the solvent is changed from benzene to DMSO in the following case : 3

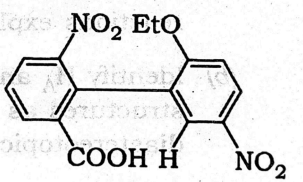


Solvent	Syn	Anti
Benzene	80%	20%
DMSO	20%	80%

(b) Predict the R/S nomenclature of the following compounds *A* and *B*. 2+1=3



(A)



(B)

Which compound will racemise readily and why?

(c) State the product of the reaction below with erythro and threo isomer of (A) : 3

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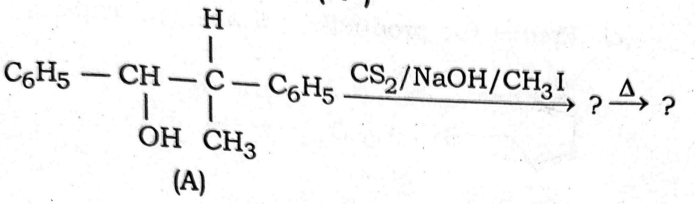

(A)

(d) Represent $CH_3COC_2H_5$ in Re-face. 1

9. (a) Explain the stereoisomerism of 6,6′-dinitrodiphenic acid and draw the energy profile diagram for racemization of its enantiomers on heating. Label each maximum and minimum with appropriate rotamers. 3

(b) Account for the fact that isomeric bromoethers (A and B) undergo solvolysis in acetic acid to give same mixture of products (C and D). 2